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(54) **Copper base alloys and terminals using the same**

(57) A copper base alloy for terminals that is of the Cu-Ni-Sn-P or Cu-Ni-Sn-P-Zn system comprising 0.5-3.0% Ni, 0.5-2.0% Sn, 0.01-0.2% P and optimally 0.01-2.0% Zn, bal. Cu, and that has a tensile strength of at least 500 N/mm^2, a spring limit of at least 400 N/mm^2, a stress relaxation of no more than 10%, a conductivity of at least 30 % IACS and a bending workability in terms of the R/t ratio of no more than 2 is provided. Terminals the spring portion or the entire part of which is produced from that copper base alloy, having an initial insertion/extraction force of 1.5 N to 30 N and a resistance of no more than 3 mΩ at low voltage and low current as initial performance, with the added characteristics that the terminals will experince not more than 20% stress relaxation are also provided. The alloy is superior to the conventional bronze, phosphor bronze and Cu-Sn-Fe-P alloys for terminals in terms of tensile strength, spring limit, stress relaxation characteristics and conductivity and, hence, the terminals manufactured from those alloys have high performance and reliability than the terminals made of the conventional copper base alloys for terminals.

0.01 – 2. Zn
0.5 – 3% Ni
0.5 – 2 Sn
0.01 – 0.2 P
Cu

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of measuring the stress relaxation characteristics of the copper base alloy for terminals of the present invention.

Fig. 6 is a graph showing the relationship between the contact load and the conditions for heat treatment in the case of measuring the stress relaxation characteristics of the copper base alloy for terminals of the present invention.

Fig. 7 is a graph showing the results of measurement of resistance at low voltage and low current in the tests of electrical performance of the copper base alloy for terminals of the present invention.

Fig. 8 is a graph showing the results of measurement of resistance at low voltage and low current in the tests of electrical performance of the copper base alloy for terminals of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In its first aspect, the present invention provides a copper base alloy for terminals that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P and the balance of Cu and incidental impurities.

In its second aspect, the present invention provides a copper base alloy for terminals that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P and the balance of Cu and incidental impurities, with the ratio of Ni to P (Ni/P) being in the range of 10 - 50 and fine precipitates of Ni-P compound in the size of no larger than 100 nm being uniformly dispersed in the alloy.

In its third aspect, the present invention provides a copper base alloy for terminals that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P and the balance of Cu and incidental impurities, with the ratio of Ni to P (Ni/P) being in the range of 10 - 50 and fine precipitates of Ni-P compound in the size of no larger than 100 nm being uniformly dispersed in the alloy, said alloy having a tensile strength of at least 500 N/mm^2. a spring limit of at least 400 N/mm^2, a stress relaxation of no more than 10%, a conductivity of at least 30 % IACS and a bending workability given in terms of the ratio of R to t (R/t) of no more than 2, where R is a bend radius and t is a thickness of the specimen.

In its fourth aspect, the present invention provides a copper base alloy for terminals that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P and 0.01 - 2.0 % Zn and the balance of Cu and incidental impurities.

In its fifth aspect, the present invention provides a copper base alloy for terminals that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P, 0.01 - 2.0 % Zn and the balance of Cu and incidental impurities, with the ratio of Ni to P (Ni/P) being in the range of 10 - 50, fine precipitates of Ni-P compound in the size of no larger than 100 nm being uniformly dispersed in the alloy.

In its sixth aspect, the present invention provides a copper base alloy for terminals that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P, 0.01 - 2.0 % Zn and the balance of Cu and incidental impurities, with the ratio of Ni to P (Ni/P) being in the range of 10 - 50, fine precipitates of Ni-P compound in the size of no larger than 10 nm being uniformly dispersed in the alloy, said alloy having a tensile strength of at least 500 N/mm^2, a sprig limit of at least 400 N/mm^2, a stress relaxation of no more than 10%, a conductivity of at least 30 % IACS and a bending workability given in terms of the ratio of R to t (R/t) of no mcre than 2, where R is a bend radius and t is a thickness of the specimen.

In its seventh aspect, the present invention provides a terminal with a built-in spring that is produced from a spring material or a terminal that is entirely made of said spring material including a spring as an integral part, said spring material being produced by melting a copper base alloy that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P and the balance of Cu and incidental impurities, said alloy being worked, after melting, by hot- and cold- rolling.

In its eighth aspect, the present invention provides a terminal with a built-in spring that is produced from a spring material or a terminal that is entirely made of said spring material including a spring as an integral part, said spring material being produced by melting a copper base alloy that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P and the balance of Cu and incidental impurities, with the ratio of Ni to P (Ni/P) being in the range of 10 - 50, fine precipitates of Ni-P compound within the size of no larger than 10 nm being uniformly dispersed in the alloy, said alloy being worked, after melting, by at least one of cold rolling and hot rolling.

In its ninth aspect, the present invention provides a terminal with a built-in spring that is produced from a spring material or a terminal that is entirely made of said spring material including a spring as an integral part, said spring material being produced by melting a copper base alloy that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P, 0.01 - 2.0 % Zn and the balance of Cu and incidental impurities, said alloy being worked, after melting, by at least one of cold rolling and hot rolling.

In its tenth aspect, the present invention provides a terminal with a built-in spring that is produced from a spring material or a terminal that is entirely made of said spring material including a spring as an integral part, said spring material being produced by melting a copper base alloy that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P, 0.01 - 2.0 % Zn and the balance of Cu and incidental impurities, with a ratio of Ni to P (Ni/P) being in the range of 10 - 50, fine precipitates of Ni-P compound within the size of no larger than 100 nm being

is too weak, separation occurs due to the vibration or an oxide film will easily form and the contact resistance is too unstable to insure satisfactory electrical reliability for connectors.

Under the circumstances, the initial insertion/extraction force of the terminal is desirably from 1.5N to 30N and, to this end, the terminal material to be used must have a tensile strength of at least 500 N/mm^2, a spring limit of at least 400 N/mm^2 and, from a view point of good moldability of terminals, a value of R/t of 2 or less. In order to obtain better bending workability, it is important that the crystal grain size is 50 µm or less, more preferably 25 µm or less.

The initial resistance at low voltage and low current is desirably small, preferably not more than 3 mΩ. The value of contact electric resistance is dependent primarily on how much the contact load on the coupling will decrease due to heat cycles. However, the stress relaxation caused by spontaneous heat generation from the material as well as the stress relaxation caused by the effects of temperature in the automobile's engine room or around the exhaust system will also reduce the contact load, which eventually leads to a higher contact electric resistance.

To avoid this problem, the terminal material itself must not undergo stress relaxation greater than 10% upon standing at 150°C for 1,000 hours, and it is also required to have a tensile strength of at least 500 N/mm^2, a spring limit of at least 400 N/mm^2, an electric conductivity of at least 30 % IACS and a stress relaxation after working into a spring of no more than 20%.

The following examples are provided for the purpose of further illustrating the present invention.

Example 1

Alloys having the compositions shown in Table 1 were melted in a high-frequency melting furnace and hot-rolled at 850°C, after heating to this temperature, to a thickness of 5.0 mm. Then, each sheet was subjected to facing to a thickness of 4.8 mm and by subsequent repitition of cold-rolling and heat treatment, sheets having a thickness of 0.2 mm were obtained at a final reduction ratio of 67%.

The tensile strength, elongation and spring limit of each sheet were measured: at the same time, the bending workability and stress relaxation characteristics of each sheet were investigated. The results are shown in Table 1 in comparison with those of conventionally used brass, phosphor bronze and Cu-Sn-Fe-P alloy.

The measurement of tensile strength, conductivity and spring limit were in accordance with JIS Z 2241, JIS H 0505 and JIS H 3130, respectively.

The bending workability of each sheet was evaluated by a 90° W bend test, in which according to CES-M0002-6 the sample was subjected to 90° W bend with a tool of R=0.1 mm and the surface state of the center ridge was evaluated by the following criteria: X, cracking occurred; △, wrinkles occurred; ○, good results. The bending axis was set to be parallel to the rolling direction.

In a stress relaxation test, the test piece was bent in an arched way such that a stress of 400 N/mm^2 would develop in the central part and the residual bend that remained after holding at 150°C for 1,000 hours was calculated as "stress relaxation" by the following formula:

$$\text{stress relaxation}(\%)=\{(L_1-L_2)/(L_1-L_0)\}X100$$

where

L_0 : the length of the tool (mm);
L_1 : the initial length of the sample (mm)
L_2 : the horizontal distance between the ends of the sample after the test (mm)

The migration test was conducted in the following way: A plate as shown in Fig. 1 (1: ABS resin; 2: opening) made of ABS resin (2 mm(t) X 16 mm(w) X 72 mm(l)) and having in the central area thereof a circular opening was sandwiched by a pair of test pieces (each 0.2 mm(t) X 5 mm(w) X 80 mm(l)) and the resulting assembly was joined together by winding around it at both upper and lower portions with separate pieces of Teflon tape. Then, the fixed assembly was held in a testing vessel filled with tap water as shown in Fig. 2 (3: Teflon tape; 4: test piece; 5: tap water; 6: testing vessel; 7: ammeter; 8: DC power source). The migration characteristics of each test piece was evaluated by measuring maximum leakage current after 8 hours' application of 14 V DC voltage.

As shown in the above results, the alloy sample Nos. 1 - 8 prepared in accordance with the present invention had a tensile strength of at least 500 N/mm^2, a spring limit of at least 400 N/mm^2 and a conductivity of at least 30 % IACS and their bending workability was also satisfactory. In addition, those samples had superior anti-stress relaxation characteristics represented by having a stress relaxation of not greater than 10% and also had superior anti-migration characteristics. It can therefore be concluded that the copper base alloys of the present invention are very advantageous for use in terminals in automobiles and other applications.

The alloy sample Nos. 9 - 11 are comparison alloys made, respectively, of phosphor bronze, brass and Cu-Sn-Fe-

Example 2

The characteristics of terminals using the copper base alloys, of the present invention are described below specifically with reference to an example. In order to evaluate the performance as a terminal, sheets of the alloys of the present invention were press formed and checked for the most important objective of the present invention, i.e., stress relaxation characteristics.

The alloys prepared in accordance with present invention were press formed into female terminals shown by 9 in Fig. 3, each being equipped with a spring 10. The terminals were subjected to a post-heat treatment in order to provide a good spring property.

The heat treatment consisted of heating at 180°C for 30 minutes in order to prevent excessive surface deterioration so that Sn plating could subsequently be performed as a surface treatment of terminals. The so treated terminals were subjected to a test for evaluating their stress relaxation characteristics. For comparison with prior art versions, female terminals made from a Cu-Sn-Fe-P alloy and a brass material were also subjected to a heat treatment under the same conditions and, thereafter, a performance test was conducted in the same manner.

The terminals had an initial insertion force ranging from 4.5 to 6.0N and their initial resistance at low voltage and low current ranged from 1.5 to 2.0 mΩ.

The stress relaxation characteristics of the terminals was tested by the following method: the male terminal was fitted into the female terminal and the assembly was subjected to a heat resistance test and the contact load was measured before and after the test. In the heat resistance test, the specimens were exPosed to 120°C for 300 hours. The test results are shown in Fig. 5. The percent stress relaxation was calculated by the following formula:

$$\text{stress relaxation}(\%)=\{(F_1-F_2)/F_1\}\times 100$$

where

F_1 : the initial contact load (N);
F_2 : the contact load after the test (N);

The female terminal made of the prior art Cu-Sn-Fe-P alloy experienced a greater drop in contact load than the female terminal made of the copper base alloy of the present invention and the stress relaxation of the former terminal was ca. 30%. The brass terminal experienced ca. 50% stress relaxation. On the other hand, the stress relaxation of the female terminal made of the copper base alloy within the scope of the present invention was ca. 12%, which satisfied the requirement for the stress relaxation of no more than 20% and hence was superior to the comparative terminals. Further, as shown in Fig. 6, the superiority of the terminals made of the alloy of the present invention was found to increase by subjecting the alloy to the heat treatment after press working.

The same samples were subjected to a test for evaluating their electrical performance by leaving them to stand at 120°C for 300 hours, and the resistance at low voltage and low current was measured according to JIS C 5402 both before and after the test. The results are shown in Fig. 7.

From the results shown above, one can clearly see that the copper base alloy of the present invention was also superior to the conventional Cu-Sn-Fe-P alloy and brass in terms of electrical performance. Also, as shown in Fig. 8, the superiority of the alloy of the present invention was found to be further improved by subjecting the alloy to the heat treatment after the press working thereof.

Female terminals shown by 9 in Fig. 4 were shaped that had a built-in spring 10 made from the copper base alloy of the present invention. The terminals were subjected to the same tests as in the case of the terminals depicted in Fig. 3 and the test results were as well as in the case of the terminals shown in Fig. 3.

The foregoing results demonstrate that the terminals using the copper base alloy of the present invention excel in performance as automotive terminals. It should, however, be noted here that the copper base alloy of the present invention and the terminals made of that alloy are also applicable, with equal effectiveness, to transportation instruments such as aircraft, ships, etc. as well as to public welfare instruments inclusive of TV, radio, computer, etc.

Table 2

Sample No.	Initial Contact Load (N)	Contact Load after 300 Hours (N)	Stress Relaxation (%)
Invention Alloy	7.9	6.8	13.9
Cu-Sn-Fe-P System Alloy	7.5	5.1	32.0

in bending workability.

Comparison alloy sample No. 26, which contains less Sn than the alloy of the present invention, is inferior in tensile strength and elasticity. If the Sn content is less than the amount defined in the present invention, satisfactory characteristics will not be obtained with respect to tensile strength and elasticity even if the contents of Ni and P are appropriate and the value of the Ni/P ratio is proper.

repetition of cold-rolling operations and heat treatments, sheets having a thickness of 0.2 mm with a final reduction ratio of 67% were obtained. In the course of executing these operations, conditions of heat treatments (age-precipitation) were varied in order to vary the sizes of precipitates and the crystal grain diameters thereof. As regards precipitates, an average diameter of the largest 10 precipitate particles determined by transmission electron microscopy, wherein the specimen being observed at three phases at the magnification of 50,000X, was shown as the size of the precipitate. Crystal grain diameters were evaluated according to JIS H 0501.

Then, with respect to the above mentioned materials, the tensile strength, elongation and spring limit were measured; at the same time, the bending workability and stress relaxation characteristics were investigated. The results are shown in Table 4 in comparison with one another.

As shown by the above results, all the alloy sample Nos. 27 - 34 prepared in accordance with the present invention had a tensile strength of no less than 500 N/mm^2, a spring limit of no less than 400 N/mm^2 and a conductivity of no less than 30% IACS, and their bending workability was also satisfactory. In addition, these samples had superior stress relaxation characteristics of no less than 10% as well as superior anti-migration characteristics.

In contrast, the alloy sample Nos. 35 - 42 prepared in accordance with the conventional method which comprises precipitates whose size exceeds 100 nm or whose crystal grain size exceeds 50 μm, showed decreased bending workability and they were inferior to the alloy of the present invention in any other characteristic properties inclusive of tensile strength, spring limit, anti-stress relaxation characteristics, and anti-migration characteristics.

ance at low voltage and low current as well as stress relaxation characteristics, and therefore the alloy has a remarkable advantage from a view point of industry.

That is, according to the present invention, there is provided a copper base alloy for use in a terminal which has an electric conductivity of as high as at least 30% IACS and also has both high tensile strength and high spring limit as well as superior stress relaxation characteristics of not higher than 10%. There is further provided a terminal which has contained in its structure a spring made of the alloy of the present invention or a terminal wholly made of the alloy of the present invention inclusive of its spring, the terminal having proper initial properties inclusive of a proper insertion power in the range of 1.5 - 30 N, a proper resistance at low voltage and low current of no more than 3 mΩ and a proper stress relaxation characteristics of no more than 20%.

Claims

1. A copper base alloy for the use in terminals that consists essentially, on a weight basis, of 0.5 - 3.0 % Ni, 0.5 - 2.0 % Sn, 0.010 - 0.20 % P, and optionally 0.01 - 2.0 % Zn, the balance being Cu and incidental impurities.

2. The copper base alloy for the use in terminals according to claim 1, with the ratio of Ni to P (Ni/P) being in the range of 10 - 50 and fine precipitates of Ni-P compound in the size of no larger than 100 nm being uniformly dispersed in the alloy.

3. The copper base alloy for the use in terminals according to claim 2, said alloy having a tensile strength of at least 500 N/mm^2, a spring limit of at least 400 N/mm^2, a stress relaxation of no more than 10%, a conductivity of at least 30% IACS and a bending workability given in terms of the ratio of R to t (R/t) of no more than 2, where R is a bend radius and t is a thickness of the specimen.

4. A spring for the use in terminals that contains a spring material being produced by melting a copper base alloy according to any one of claims 1 to 3, said alloy being worked, after melting, by at least one of cold rolling and hot rolling.

5. A terminal with a built-in spring that is produced from a spring material or a terminal that is entirely made of said spring material including a spring as an integral part, said spring material being produced by melting a copper base alloy according to any one of claims 1 to 3, said alloy being worked, after melting, by at least one of cold rolling and hot rolling.

6. The terminal according to claim 5 for the use as a connector terminal in automobiles and other applications.

FIG. 1

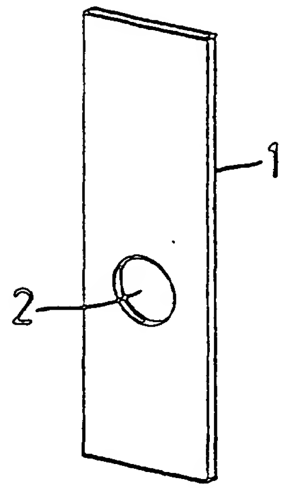


FIG. 2

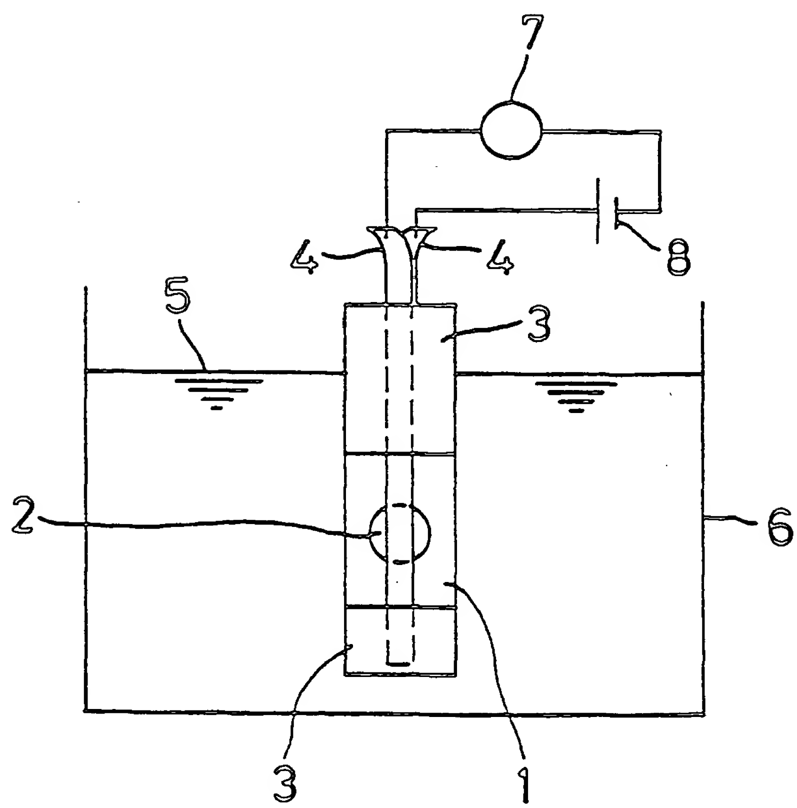


FIG. 3

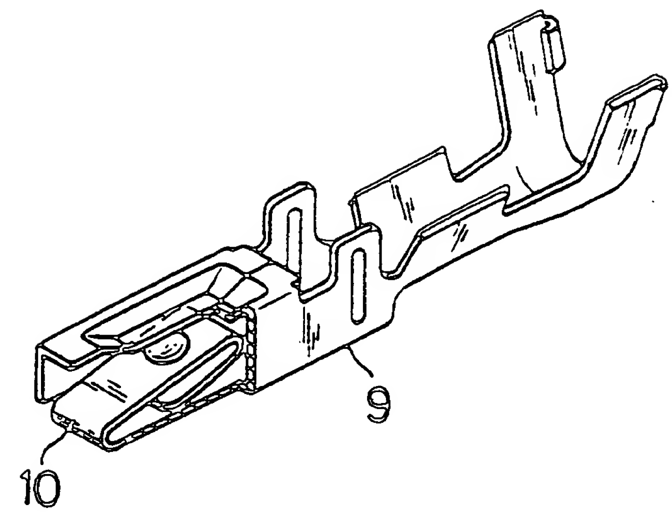


FIG. 4

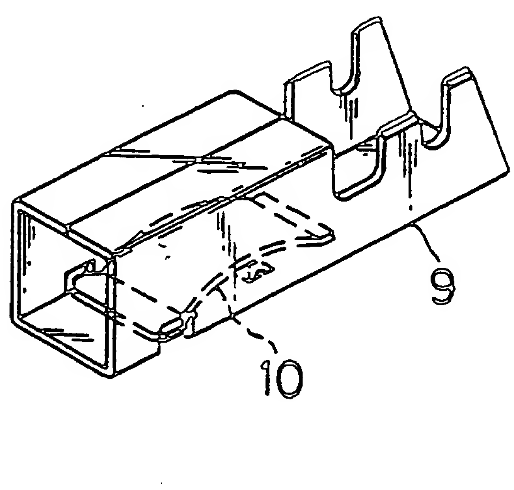
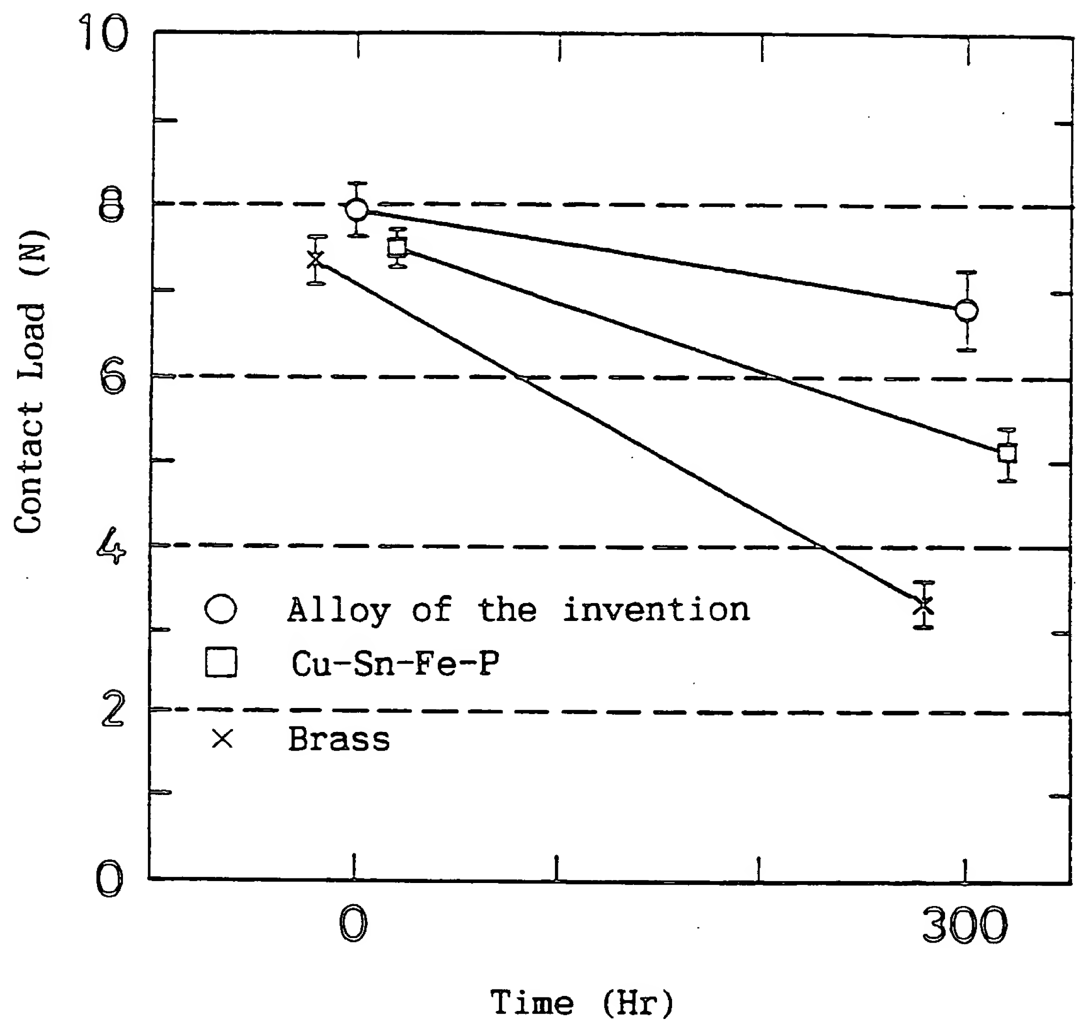
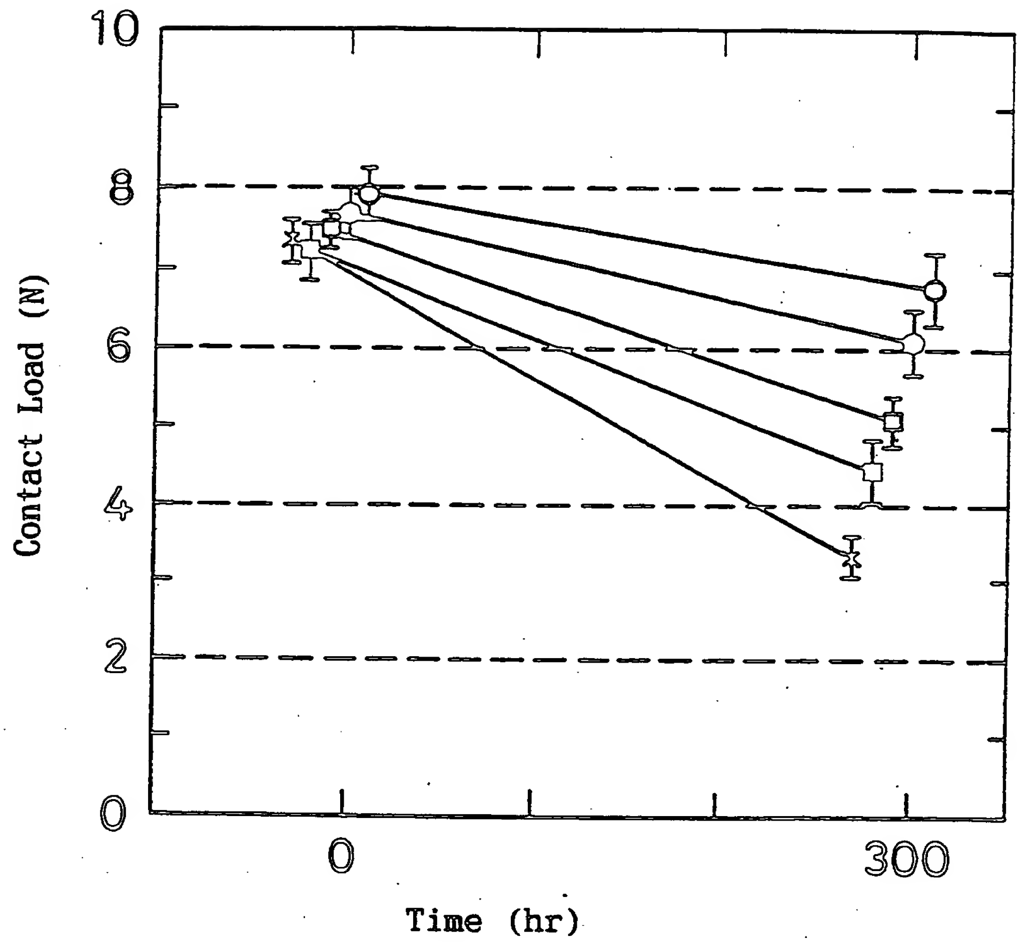


FIG. 5



10
8
6
4
2
0
Contact Load (N)
0
300
Time (Hr)
Alloy of the invention
Cu-Sn-Fe-P
Brass

FIG. 6



○ Alloy of the Invention (Heat treated after pressing)
○ Alloy of the Invention (Non-heat treated after pressing)
□ Cu-Sn-Fe-P alloy (Heat treated after pressing)
□ Cu-Sn-Fe-P alloy (Non-heat treated after pressing)
× Brass

FIG. 7

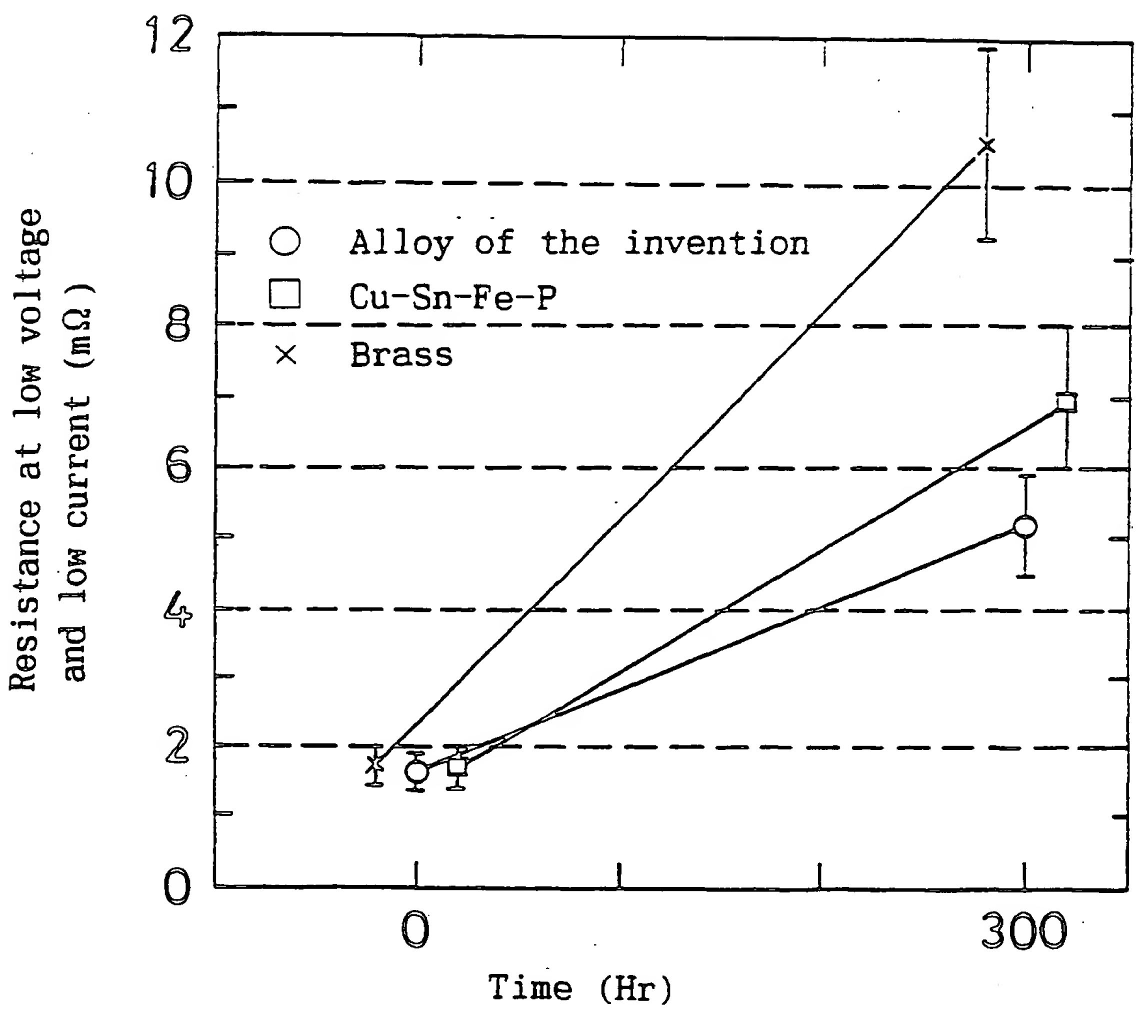
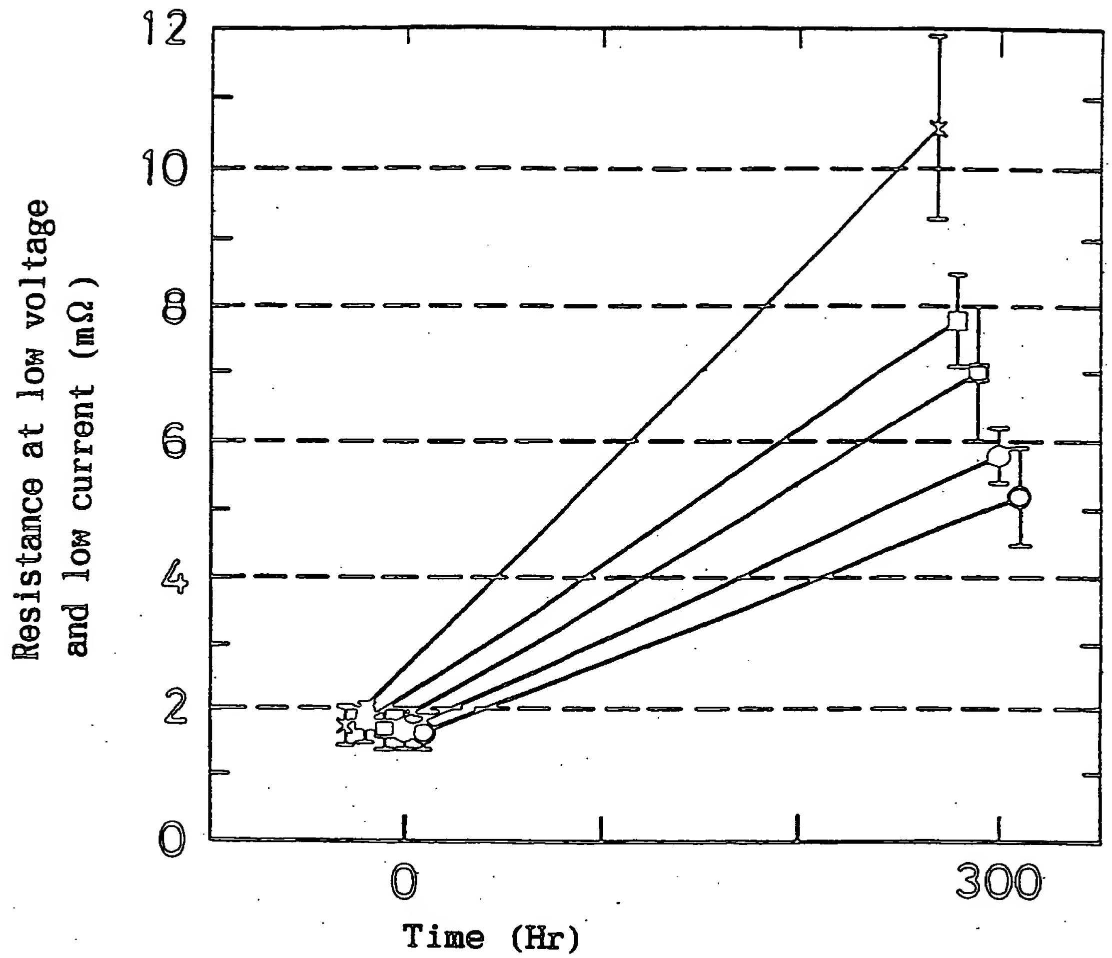

12
10
8
6
4
2
0
Resistance at low voltage and low current (mΩ)
Alloy of the invention
Cu-Sn-Fe-P
Brass
0
300
Time (Hr)

FIG. 8



○ Alloy of the Invention (Heat treated after pressing)

○ Alloy of the Invention (Non-heat treated after pressing)

□ Cu-Sn-Fe-P alloy (Heat treated after pressing)

□ Cu-Sn-Fe-P alloy (Non-heat treated after pressing)

× Brass

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EUROPEAN SEARCH REPORT

Application Number
EP 98 10 2539

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 387 293 A (ENDO TAKAYOSHI ET AL) 7 February 1995 * claims *	1-6	C22C9/06 C22C9/02
X	US 5 322 575 A (ENDO TAKAYOSHI ET AL) 21 June 1994 * claims *	1-6	
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 004, 30 April 1996 & JP 07 331363 A (NIKKO KINZOKU KK), 19 December 1995, * abstract *	1	
X	PATENT ABSTRACTS OF JAPAN vol. 008, no. 085 (C-219), 18 April 1984 & JP 59 006346 A (FURUKAWA DENKI KOGYO KK), 13 January 1984, * abstract *	1	
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 443 (C-0985), 16 September 1992 & JP 04 154942 A (DOWA MINING CO LTD;OTHERS: 01), 27 May 1992, * abstract *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 115 (C-0696), 5 March 1990 & JP 01 316432 A (DOWA MINING CO LTD), 21 December 1989, * abstract *	1	
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 123 (C-0816), 26 March 1991 & JP 03 006341 A (DOWA MINING CO LTD), 11 January 1991, * abstract *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	7 May 1998	Ashley, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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